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Structure and Properties of Polymers and Organosilanes
Adsorbed Onto Oxidized Aluminum and Titanium

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The structure of films formed by γ-aminopropyltriethoxysilane (γ-APS) adsorbed onto titanium, iron, and aluminum from aqueous solutions was determined and related to the effectiveness of the silane as a primer for improving the hydrothermal stability of metal-to-metal adhesive joints. In all cases γ-APS was adsorbed as highly hydrolyzed oligomers and then condensed during drying on the metal surface to form siloxane polymers. However, the oxidized surfaces of aluminum and, to a slight extent, iron were etched

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in aqueous solutions of γ-APS at pH 10.4, resulting in the inclusion of metal ions in the adsorbed films. Some evidence for the formation of aluminosiloxane polymers during adsorption of γ-APS onto aluminum substrates at pH 10.4 was obtained.

γ-APS was an extremely effective primer for metal/epoxy lap joints prepared from titanium, iron, and aluminum. Titanium/epoxy lap joints prepared from primed adherends had an average breaking stress of about 1750 psi after 60 days immersion in water at 60°C. Joints prepared from unprimed adherends had a breaking stress of only about 960 psi after similar hydrothermal aging.

Somewhat similar results were obtained for iron substrates. Joints prepared from unprimed adherends retained only about 25% of their initial strength after 60 days immersion in water at 60°C. By comparison, iron/epoxy lap joints prepared from adherends primed at pH 10.4 and 8.0 retained about 50% and 70%, respectively, of their initial strength after hydrothermal aging.

The breaking strengths of aluminum/epoxy lap joints prepared from unprimed adherends and from adherends primed at pH 8.5 were about 1000 psi and 1600 psi, respectively, after 40 days in water at 60°C. When unprimed aluminum/epoxy lap joints were aged in water at 23°C, corrosion was significant and the strength of the joints fell to nearly zero after about ten days. γ-APS primers inhibited such corrosion, especially when the primers were heat treated prior to bonding, causing the failure of the joints to be cohesive in the adhesive even after 60 days immersion at 23°C

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I. Introduction

One of the most important limitations regarding the use of adhesive bonding for joining metals concerns the adverse effects of water. It is well known that even the most carefully prepared adhesive joints will gradually weaken and eventually fail near the interface after prolonged exposure to water, especially at elevated temperatures. As a result, there has been a great deal of interest in developing techniques for improving the hydrothermal stability of metal-to-metal adhesive joints.

One approach to this problem has been to pretreat the metal so as to produce an oxide that is particularly stable in the presence of water. This technique has been used successfully for aluminum and titanium substrates.

An alternative is to modify the oxidized metal surface using an organic material as a primer. It is well known that the wet strength of glass fiber reinforced composites is greatly improved when the glass fibers are pretreated with a dilute aqueous solution of an organosilane "coupling agent" (1). The purpose of this research is to determine the applicability of organosilanes as "primers" for improving the hydrothermal stability of metal-to-metal adhesive joints.

Several theories have been proposed to describe the mechanisms by which silanes function as coupling agents on glass (1). Perhaps the most widely accepted is the so-called chemical bonding theory (see Figure 1). This theory considers that silane coupling agents function by forming stable covalent bonds

with both the substrate and an adhesive applied to the substrate. However, there is little direct evidence to support this theory. An additional objective of this research is to determine the mechanisms by which silanes function as coupling agents or primers for improving the hydrothermal stability of metal-to-metal adhesive joints.

The usefulness of organofunctional silanes as primers for improving the hydrothermal stability of metal-to-metal adhesive joints was determined by immersing metal/epoxy lap joints in water at 60°C and determining the strength retained as a function of immersion time. The mechanisms by which silanes function as primers was determined by using surface analysis techniques such as reflection-absorption infrared spectroscopy (RAIR), ellipsometry, and x-ray photoelectron spectroscopy (XPS) to determine the structure of thin films formed by silanes adsorbed onto metal mirrors from dilute aqueous solutions and by using scanning electron microscopy (SEM) to determine the morphological features of the fracture surfaces of lap joints.

Lap joints are, of course, widely used to evaluate adhesives and substrate pretreatments. The stress distribution in lap joints has been discussed by several authors (2,3). Surface analysis techniques such as RAIR (4,5), ellipsometry (6), and XPS (7) have also been thoroughly discussed in the literature. Accordingly, no further discussion will be given here.

II. Experimental

Sample mirrors for surface analysis were prepared by mechanically polishing enameling iron (Armco, Inc.), titanium-6Al, 4V (Timet, Inc.), and 2024 aluminum alloy (Alcoa, Inc.). Films were formed on freshly polished mirrors by immersing the mirrors in 1% aqueous solutions of γ-aminopropyltriethoxysilane (γ-APS, Union Carbide Corp.) for appropriate times, removing the mirrors from the solution, and blowing the excess solution off the mirrors using a strong stream of nitrogen. In some cases, hydrochloric acid was added to the γ-APS solutions to lower the pH.

Infrared spectra of films formed by γ-APS adsorbed onto iron, titanium, and aluminum mirrors were obtained using a Perkin-Elmer Model 180 infrared spectrophotometer and external reflection accessories from Harrick Scientific. XPS spectra were obtained using a Physical Electronics x-ray photoelectron spectrometer and magnesium K_α radiation. Ellipsometry was performed using a Rudolph Research Model 436 ellipsometer.

Lap joints were prepared according to ASTM standard D1002. Metal adherends (1 x 4 x 0.063") were mechanically polished, rinsed repeatedly, and dried. Pairs of adherends were then bonded together using an adhesive consisting of an epoxy resin (Epon 828, Shell Chemical Co.) and 9.4 weight percent of a tertiary amine catalyst (Ancamine K-61B, Pacific Anchor Chemical Co.). In some cases, the adherends were pretreated with a γ-APS primer as described above. In all cases, the lap joints were immersed in water at 60°C. At various intervals,

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joints were removed from the water, dried, and tested using an Instron Universal Testing Device to determine the breaking strength. In some cases, a Cambridge 600 scanning electron microscope was used to examine the fracture surfaces.

III. Results and Discussion

A. Titanium substrates

The infrared spectrum shown in Figure 2A was obtained from films formed by γ-APS adsorbed onto titanium mirrors as described above. The spectrum is characterized by a strong band near 1070 cm^{-1} that is assigned to an SiOSi stretching vibration, indicating that the adsorbed γ-APS was in fact highly hydrolyzed and polymerized on the surface to form a siloxane polymer. The bands observed near 1570, 1470, and 1300 cm^{-1} have been the subject of considerable debate (8,9). However, we have recently shown that these bands are related to the formation of amine bicarbonate species by adsorbed carbon dioxide (10,11). Accordingly, the bands near 1570 and 1470 cm^{-1} are assigned to the deformation modes of protonated amino (NH_3) groups while the band near 1300 cm^{-1} is assigned to the symmetric stretching mode of bicarbonate ions (12).

The as-formed films were stable in a dry atmosphere but during exposure to the laboratory atmosphere several changes were noted (see Figures 2B and 2C). The band originally observed near 1070 cm^{-1} gradually split into components near 1040 and 1130 cm^{-1}, indicating additional polymerization of the adsorbed γ-APS. The band initially observed near 1470 cm^{-1} decreased in intensity and the band near 1300 cm^{-1} increased in frequency to about 1330 cm^{-1}, indicating some rearrangement of the absorbed carbon dioxide.

The spectrum shown in Figure 3 was obtained from mirrors that were immersed in 1% aqueous solutions of γ-APS at pH 10.4,

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withdrawn, dried in a stream of nitrogen, and then heat treated in an oven at 100°C for twenty minutes. The bands near 1570, 1470, and 1300 cm^{-1} are not observed, indicating that the absorbed carbon dioxide is easily removed by relatively mild heating. Moreover, the band near 1130 cm^{-1} has increased in frequency somewhat to about 1145 cm^{-1} and the band near 1040 cm^{-1} has become more prominent, indicating additional polymerization of the film.

The spectra shown in Figure 4 were obtained from films formed by γ-APS adsorbed onto titanium mirrors from 1% aqueous solutions that were acidified by addition of HCl. These spectra are dominated by an intense band near 1120 cm^{-1} that is assigned to an SiOSi stretching mode, again indicating formation of siloxane polymers. The weaker bands near 1600 and 1500 cm^{-1} are assigned to the deformation modes of amino groups that are protonated as amine hydrochlorides.

The stability of the air-formed oxide on titanium mirrors during immersion in aqueous solutions of γ-APS has also been considered. Several mirrors were polished as described above and then heated in air at 300°C for one hour. Results obtained from ellipsometry indicated that the oxide on the mirrors was about 150 A in thickness. RAIR spectra from such mirrors were characterized by an absorption band near 850 cm^{-1} that was assigned to the rutile form of TiO_2 (13). The intensity of the oxide band near 850 cm^{-1} was then determined as a function of immersion time in 1% aqueous solutions of γ-APS at pH 10.4 (see Figure 5). The results obtained indicated that the air-formed

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oxide on the titanium mirrors was stable during immersion in such solutions. Similar results were obtained at pH 5.5

At least some aspects of the chemical bonding theory can be substantiated. There is no doubt that γ-APS is hydrolyzed in aqueous solutions and then polymerizes after adsorption onto titanium mirrors to form siloxane polymers. However, no evidence for the formation of primary bonds between γ-APS and the oxidized surface of titanium was obtained from infrared spectroscopy even when films approximately a monolayer in thickness were considered. Moreover, the air-formed oxide on titanium mirrors was stable in aqueous solutions of γ-APS. Accordingly, it was tentatively concluded that γ-APS interacts with the oxidized surface of titanium by hydrogen bonding.

The use of γ-APS as a primer for titanium/epoxy lap joints has also been considered. The results are shown in Figure 6. In all cases, the strength of the lap joints decreased slowly as a function of immersion time in water at 60°C. However, γ-APS was an extremely effective primer. Joints prepared from unprimed adherends had an average shear stress of approximately 960 psi after sixty days immersion time. Joints prepared from adherends primed with γ-APS at pH values of 10.4 and 8.0 had breaking stresses of approximately 1750 psi after similar aging in water at elevated temperatures.

It is interesting to note that titanium/epoxy lap joints prepared from adherends primed with γ-APS at pH 5.5 had lower breaking stresses after water immersion than joints prepared from adherends primed at pH 10.4 and 8.0. Opposite behavior has

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been observed for iron/epoxy lap joints (see below). In that case, joints prepared from adherends primed with γ-APS at pH 8.0 had substantially greater breaking stresses after water immersion than did joints prepared from adherends primed at pH 10.4 (4,10).

Reference to Figure 6 also indicates that the initial breaking strength of titanium/epoxy lap joints was increased substantially when the primer was dried at 100°C for twenty minutes prior to adhesive bonding. However, after extensiv water immersion, the strength of joints prepared from primec heat-treated adherends approached that of joints prepared fro adherends that were primed but not heat-treated.

Visual inspection of the fracture surfaces of the titanium/epoxy lap joints provided some insight into the mechanisms by which γ-APS primers function on titanium adherends. Unprimed joints always failed very near the interface with a small patch of adhesive near the end of each adherend (see Figure 7A). Such behavior is characteristic of lap joints (14) and is related to the large peeling stresses near the ends of a lap joint. The fracture surfaces of primed joints were similar in that failure occurred near the interface and that a small patch of adhesive was left near the end of each adherend (see Figure 7B and 7C). However, it was clear that failure of the primed joints was mostly within the adhesive even after long immersion times.

γ-APS is adsorbed from aqueous solutions onto titanium as highly hydrolyzed oligomers that polymerize on the surface to

form siloxane polymers. Since γ-APS is adsorbed from solution and then polymerized, it interacts with the oxide more completely than the relatively viscous adhesive. The polymerized γ-APS interacts with the adhesive by interpenetration and by chemical reaction with the epoxy groups of the adhesive. The result is a modified interphase that causes the locus of failure to shift from near the interface for unprimed adherends to within the adhesive for primed adherends.

Results obtained here indicate that γ-APS is less effective as a primer for titanium/epoxy lap joints when applied from solutions acidified to pH 5.5. However, the opposite behavior has been observed for iron/epoxy lap joints (4,10). The reasons for this behavior are not presently known but are important for an understanding of the mechanisms by which silanes function and are being investigated further.

B. Iron substrates

We have previously shown that γ-APS is an extremely effective primer for improving the hydrothermal stability of iron/epoxy adhesive bonds (4,10). It is very interesting to compare the results obtained for iron substrates with those described above for titanium substrates.

The structures of films formed by γ-APS adsorbed onto iron and titanium mirrors are very similar. Infrared spectra of the films formed on iron are nearly identical to spectra of films forned on titanium (see Figure 4). Accordingly, it has been concluded that γ-APS is adsorbed onto iron mirrors to form

siloxane polymers. When the adsorption is carried out from solutions acidified by addition of HCl, the amino groups are protonated as hydrochlorides. When adsorption occurs at pH 10.4, many of the amino groups form bicarbonate species with absorbed carbon dioxide. Little evidence for primary bonding between γ-APS and the oxidized surface of iron has been obtained using RAIR and XPS. As a result, it is presently considered that the principal interaction between γ-APS and iron (oxides) involves hydrogen onding. However, this conclusion is preliminary and may require revision (see below).

We have, however, obtained some evidence that the oxidized surface of iron can be lightly etched in aqueous solutions of γ-APS at pH 10.4. A pair of iron mirrors was oxidized in air at 300°C for 15 minutes to produce an oxide about 225 A in thickness and probably consisting of Fe_3O_4 and α-Fe_2O_3 (15). The RAIR spectrum of the oxide was characterized by a band near 650 cm^{-1} and by shoulders near 700 and 600 cm^{-1} (see Figure 8A). The spectrum shown in Figure 8B was obtained after the same mirrors were immersed in a 1% aqueous solution of γ-APS at pH 10.4 for 30 minutes, rinsed in distilled water, and then blown dry in nitrogen. When the spectrum shown in Figure 8B was substracted from that shown in Figure 8A, it was observed that the shoulder near 600 cm^{-1} was reduced in intensity (see Figure 8C) but the bands near 700 and 650 cm^{-1} were not. These results probably indicate that α-Fe_2O_3 is selectively etched and that films formed by γ-APS adsorbed onto iron from aqueous solutions at pH 10.4 may contain small numbers of metal ions.

Accordingly, the actual structures of films formed by γ-APS adsorbed onto iron and titanium at pH 10.4 are probably slightly different. The structures of films formed by γ-APS adsorbed onto iron and titanium mirrors from aqueous solutions at pH 8.0 are considered to be very similar since neither substrate was etched at pH 8.0.

The breaking strength of iron/epoxy lap joints is shown as a function of immersion time in water at 60°C in Figure 10. It is evident that the hydrothermal stabilities of iron/epoxy and titanium/epoxy joints are very different. The breaking strength of iron/epoxy lap joints always decreased rapidly during the first ten days of immersion and then continued to decrease at a much slower rate for times as long as 60 days. As indicated above, the breaking strength of titanium/epoxy lap joints decreased only slowly during immersion in water at 60°C for times as long as 60 days (see Figure 6).

However, γ-APS was an extremely effective primer for iron/epoxy lap joints. Joints prepared from unprimed adherends retained only about 25% of their initial strength after 60 days immersion at 60°C. Joints prepared from adherends primed with γ-APS at pH 10.4 retained about 50% of their strength after 60 days but joints prepared with γ-APS primer at pH 8.0 retained about 70% of their strength after such immersion. γ-APS was thus a much better primer for iron/epoxy lap joints when applied from acidified solutions. Little pH effect was observed for titanium/epoxy lap joints although the γ-APS primer was somewhat less effective when applied from strongly acidified solutions.

These results indicate that the failure mechanisms of iron/epoxy and titanium/epoxy lap joints are very different. Moreover, it is evident that the mechanisms by which γ-APS functions as a primer are very different for iron and titanium substrates even though γ-APS is an extremely effective primer for both substrates.

We have previously shown that the failure of iron/epoxy lap joints immersed in water at 60°C for long times is consistent with a model suggesting debonding of the adhesive a certain distance into the joint when a critical concentration of water is obtained that same distance into the joint (10). Some information has now been obtained regarding the debonding reaction.

Considering that the breaking strength of titanium/epoxy lap joints decreases only very slowly during immersion in water at 60°C, it is evident that both the oxide on titanium and the adhesive used to prepare the lap joints are rather stable to the effects of water. The failure of iron/epoxy lap joints must result from a transformation in the oxide, or perhaps, from hydrolysis of interfacial bonds. Corrosion of the substrate is the most obvious explanation for the degradation of iron/epoxy adhesive joints during hydrothermal aging. However, corrosion is not considered to be an important factor for the iron/epoxy system considered here. Corrosion products are not readily observed on the fracture surfaces of iron/epoxy lap joints that have been immersed in water at 60°C for long periods of time. Moreover, if corrosion was a significant factor, elimination of

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either the anodic or cathodic reaction should reduce the rate at which lap joints deteriorate during hydrothermal aging. The reduction of oxygen according to

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
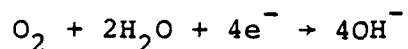
was considered to be the most likely cathodic reaction. However, when a set of iron/epoxy lap joints was aged in deoxygenated water at 60°C, the breaking strength decreased as a function of immersion time in a way similar to that shown in Figure 10 for hydrothermal aging in the presence of oxygen.

The most likely reasons for the deterioration of iron/epoxy lap joints during hydrothermal aging are hydrolysis of interfacial bonds and hydration of the oxide. In that regard, it is interesting to consider results recently obtained by Smith (16) for crack propagation during wedge testing of steel/epoxy adhesive joints. Smith regards the oxidized surface of steel as having certain surface sites that are unoccupied or else are occupied by OH^- or O^{-2} ions. Unoccupied surface sites adsorb adhesive weakly but surface sites occupied by OH^- and O^{-2} ions strongly adsorb acidic functional groups of the adhesive. During hydrothermal exposure, there is no thermodynamic driving force for degradation if the surface sites are occupied by OH^- ions. If the surface sites are occupied by O^{-2} ions, a slow degradation reaction can occur. However, if the surface sites are unoccupied, rapid degradation may be obtained.

This model may be applied to the iron/epoxy lap joints

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considered here as follows. When no primer is used, the surface sites may be unoccupied, leading to rapid loss of joint strength during hydrothermal exposure. When the adherends are primed with γ-APS at pH 10.4, surface sites may be occupied by NH_2 groups. The strength of lap joints prepared from such adherends decreases slowly during exposure to water at elevated temperatures. If adherends are primed with acidified solutions of γ-APS, the surface sites may be occupied by SiO^- groups. In this case, the strength of iron/epoxy lap joints decreases very slowly during hydrothermal aging.

Obviously, more work needs to be done in order to determine the extent to which the above model applies to iron/epoxy lap joints prepared using γ-APS primers. However, some support for the model was obtained from analysis of the fracture surfaces (see Figure 11). Under dry conditions, the iron/epoxy lap joins always failed cohesively within the adhesive. However, after prolonged hydrothermal aging unprimed joints failed very near the interface. The failure of joints prepared from adherends primed with γ-APS at pH 10.4 and 8.0 was substantially cohesive within the adhesive even after immersion in water at 60°C for 60 days.

C. Aluminum substrates

The interaction of γ-APS with the oxidized surface of 2024 aluminum alloy has been reported previously (5). The results obtained indicated that the surface was rapidly etched in dilute aqueous solutions of γ-APS at pH 10.4 (see Figure 12A).

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However, the rate of etching was reduced as the pH was reduced. Little dissolution of the oxide was noted at pH 6.8 (see Figures 12B and 12C). An accumulation of copper near the surface was observed during etching of the oxide at high pH values using XPS (5).

Infrared spectra of films formed by γ-APS adsorbed onto aluminum mirrors from aqueous solutions acidified to pH 6.8 were similar to those previously reported for iron and titanium substrates at similar pH values (see Figure 13A). Such spectra were characterized by absorption bands near 1600 and 1500 cm^{-1} that were assigned to protonated amino (NH_3^+) groups, indicating formation of an amine hydrochloride, and by a strong band near 1120 cm^{-1} that was assigned to an SiOSi stretching vibration, indicating formation of a siloxane polymer on the surface.

Infrared spectra of films formed by γ-APS adsorbed onto aluminum from aqueous solutions at higher pH values were quite different from those formed on iron and titanium, reflecting the dissolution of aluminum oxides obtained under such conditions (see Figures 13B, C, and D). Films formed by adsorption of γ-APS onto aluminum mirrors at pH 8.5 also formed hydrochlorides as evidenced by the bands near 1600 and 1500 cm^{-1}. However, the siloxane stretching mode was observed near 1080 cm^{-1}. As indicated earlier, this mode is usually observed near 1120 or 1130 cm^{-1} for γ-APS films on iron and titanium and for γ-APS films formed on aluminum under conditions where little dissolution of the oxide occurs. The band near 1080 cm^{-1} for films formed on aluminum at pH 8.5 may be attributed to

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formation of an aluminosiloxane polymer. The infrared spectra of films formed on aluminum at pH 10.4 depended markedly on the adsorption time. Films formed during a one minute adsorption were similar to those formed on iron and titanium at pH 10.4. However, films formed during 15 minutes adsorption at pH 10.4 were characterized by an infrared band near 1060 cm^{-1}, again indicating dissolution of the oxide and the likely formation of an aluminosiloxane polymer.

Y-APS has been found to be an effective primer for improving the hydrothermal stability of aluminum/epoxy lap joints. The breaking strength of such adhesive joints is shown as a function of immersion time in water at 60°C in Figure 14. Joints prepared from unprimed adherends had an average shear stress of about 1000 psi after 40 days immersion. By comparison, the breaking stress of joints prepared from adherends primed with Y-APS at pH 10.4 for 1 minute and for 15 minutes had breaking stresses of about 1300 and 1500 psi, respectively. Joints prepared from adherends primed at pH 8.5 were very slightly stronger than those prepared from adherends primed at pH 10.4 for 15 minutes and had breaking stresses of about 1600 psi after 40 days immersion in water at 60°C.

Another set of lap joints was prepared and exposed to water at 23°C for times as long as 60 days. The average shear stress is shown as a function of immersion time for such joints in Figure 15. In this case, corrosion of unprimed joints was significant and the strength of unprimed joints fell to negligibly small values after 10 days immersion. Corrosion was

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much less significant on primed joints. Lap joints prepared from adherends primed with γ-APS at pH 10.4 for 1 minute had an average breaking stress of about 900 psi after 60 days immersion. Joints prepared from adherends primed with γ-APS at pH 8.5 were the strongest after 60 days and had breaking stresses of about 1250 psi. The performance of joints prepared from adherends primed at pH 10.4 for 15 minutes was comparable to that of joints prepared from adherends primed at pH 8.5 but some tendency for such joints to weaken after 60 days immersion was noted.

Corrosion of the substrate was the cause of failure of aluminum/epoxy lap joints immersed in water at 23°C for extended periods of time. However, γ-APS primers were extremely effective in reducing such corrosion. As shown in Figure 16, the fracture surfaces of joints prepared from primed adherends exhibited much less corrosion than those of joints prepared from unprimed adherends. γ-APS primers were especially effective for inhibiting the corrosion of aluminum adherends when the primer films were heat treated in air at 100°C for 20 minutes prior to adhesive bonding. In such cases, the average shear stress of the aluminum/epoxy lap joints was essentially unchanged even after 40 days immersion at 23°C. Virtually no corrosion was observed on the fracture surfaces of such joints, demonstrating the corrosion inhibiting effectiveness of γ-APS primers.

V. Conclusions

The results obtained here indicate that γ-aminopropyltrieth-oxysilane (γ-APS) is an extremely effective primer for improving the hydrothermal stability of metal-to-metal adhesive joints prepared from titanium, iron, and aluminum adherends. However, the optimum conditions for applying the primers vary according to the substrate and reflect the different mechanisms by which aqueous solutions of γ-APS interact with the oxides and the different failure mechanisms obtained for the adherends considered here. Thus, depending on the substrate, it may be beneficial to acidify the solution from which the primer is applied or to heat treat the primer film prior to adhesive bonding. γ-APS primers should be extremely useful in applications where other pretreatments such as etching and anodization are inappropriate. However, these primers may be most useful when applied after an etching or anodization pretreatment. This possibility is presently being investigated.

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R—Si—|—R'|₃

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R—Si—|—OH|₃

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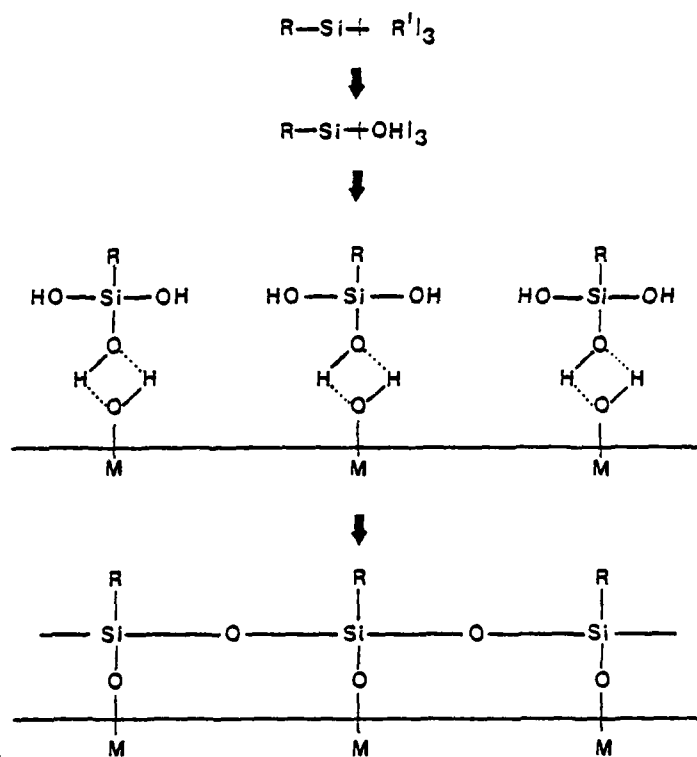
Figure 1. Chemical bonding theory of mecha-
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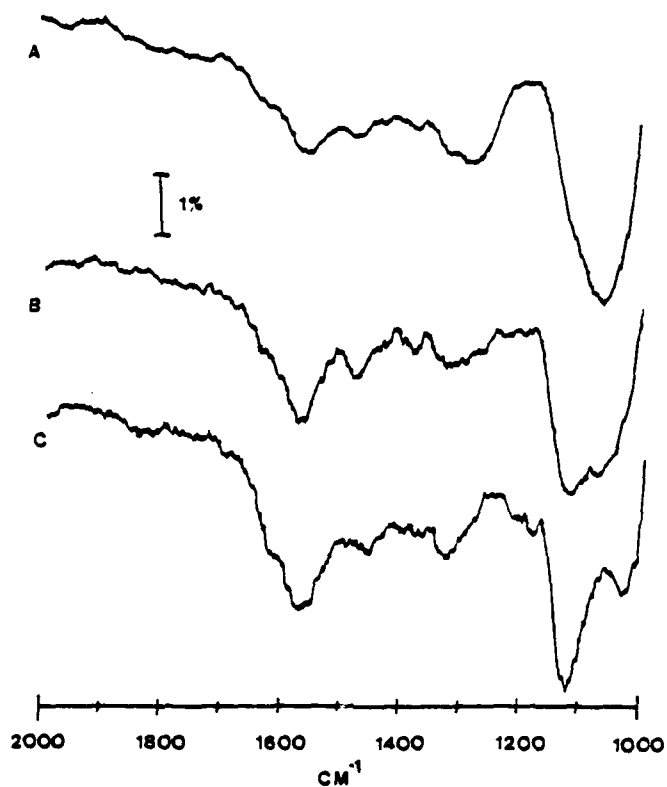
Figure 2. Infrared spectra of thin films
formed by γ-APS adsorbed onto ti-
tanium mirrors from 1% aqueous
solutions at pH 10.4: (A) - as
formed, (B) - after five hours ex-
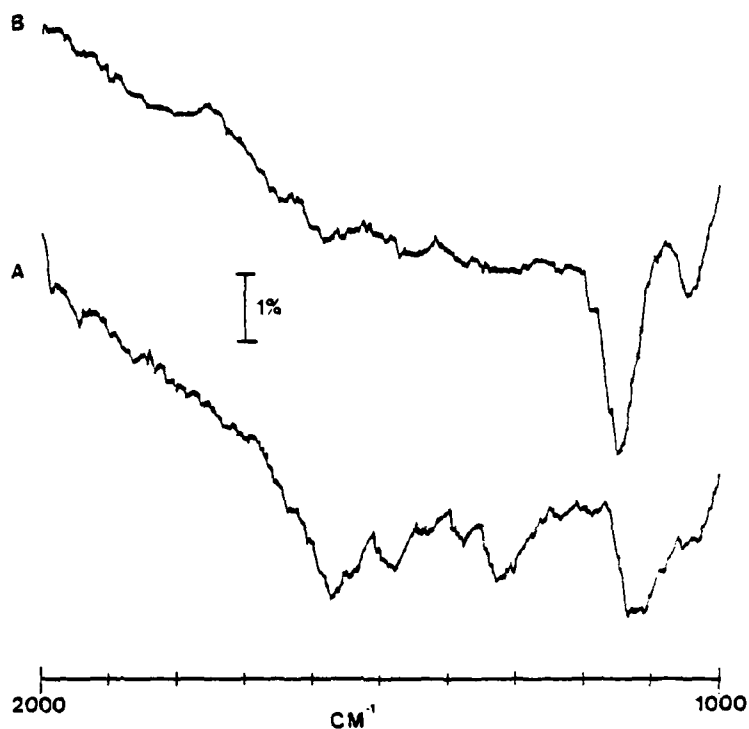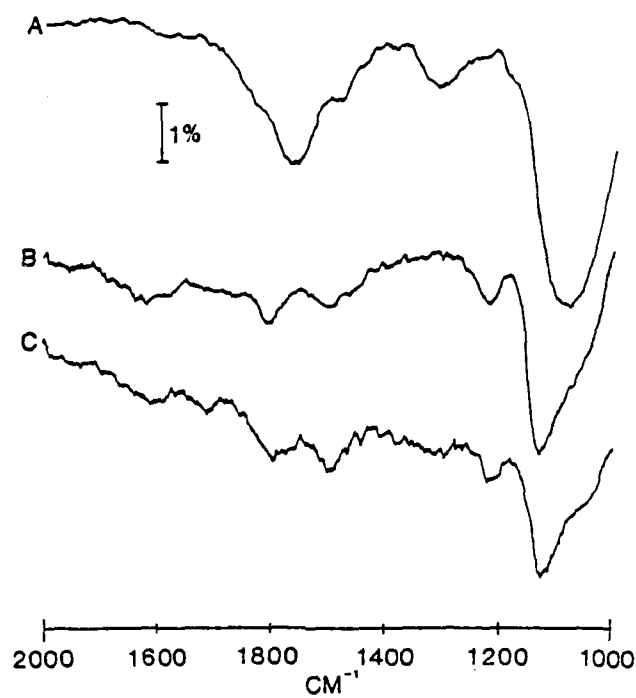posure to the laboratory atmosphere,
and (C) - after three days exposure.

Figure 3. Infrared spectra of thin films formed
by γ-APS adsorbed onto titanium mir-
rors from 1% aqueous solutions at
pH 10.4: (A) - before and (B) - af-
ter heat treating at 100°C for 20
minutes.

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Figure 4.   Infrared spectra of thin films
formed by γ-APS adsorbed onto
titanium mirrors from 1% aqueous
solutions at (A) - pH 10.4, (B) -
pH 8.5, and (C) - pH 5.5.
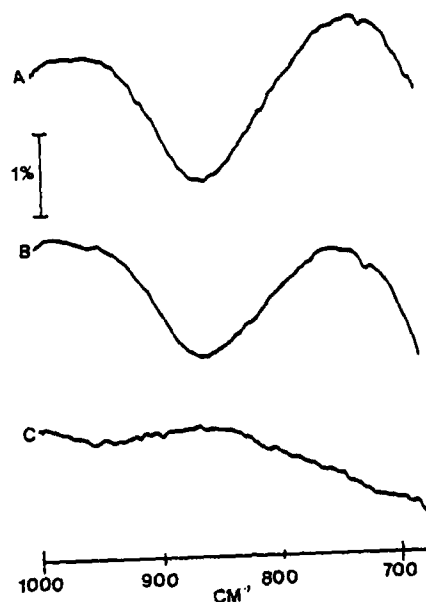
Figure 5. Effect of immersion in 1% aqueous solution of γ-APS at pH 10.4 on infrared spectra of oxide on titanium mirrors: (A) - before immersion, (B) - after immersion for thirty minutes, and (C) - difference.
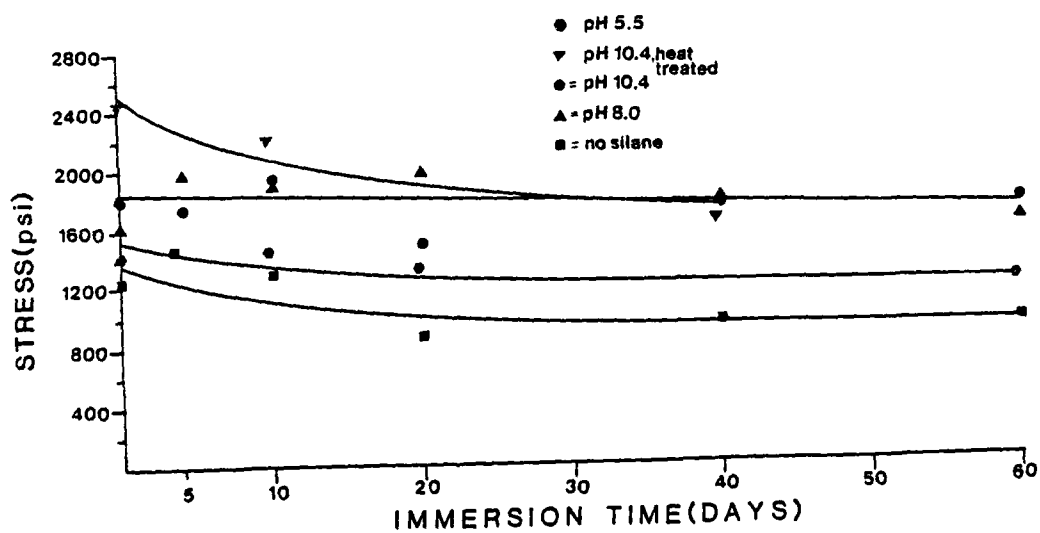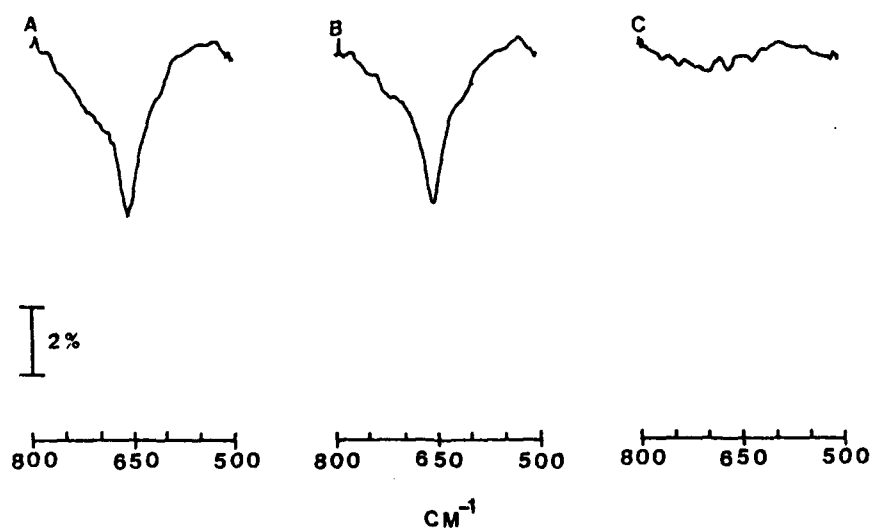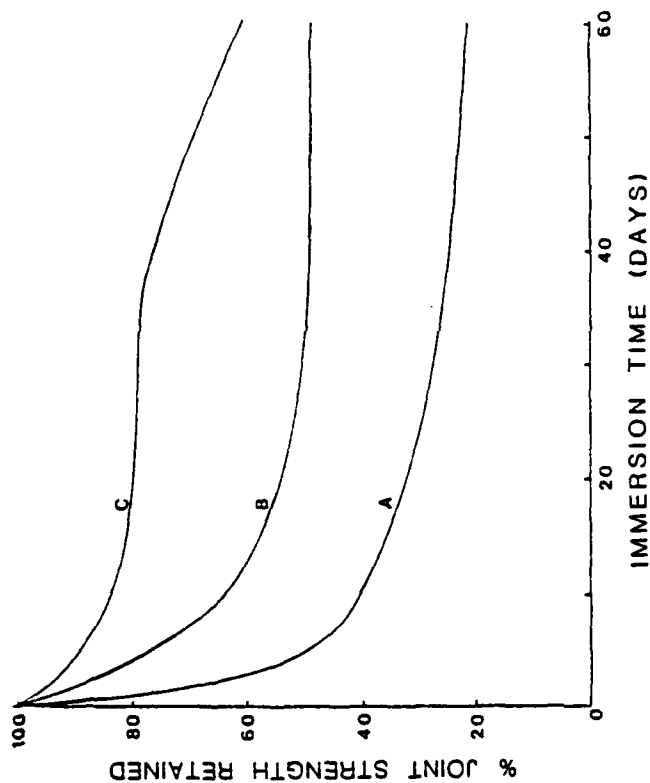

Figure 6. Breaking strength versus immersion time in water at 60°C for titanium/epoxy lap joints.

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Figure 7. Fracture surfaces of titanium/epoxy lap joints. Samples A (no primer) and B (γ-APS primer at pH 10.4) were fractured without immersion in water. Samples C (no primer) and D (γ-APS primer at pH 10.4) were fractured after 60 days in water at 60°C.

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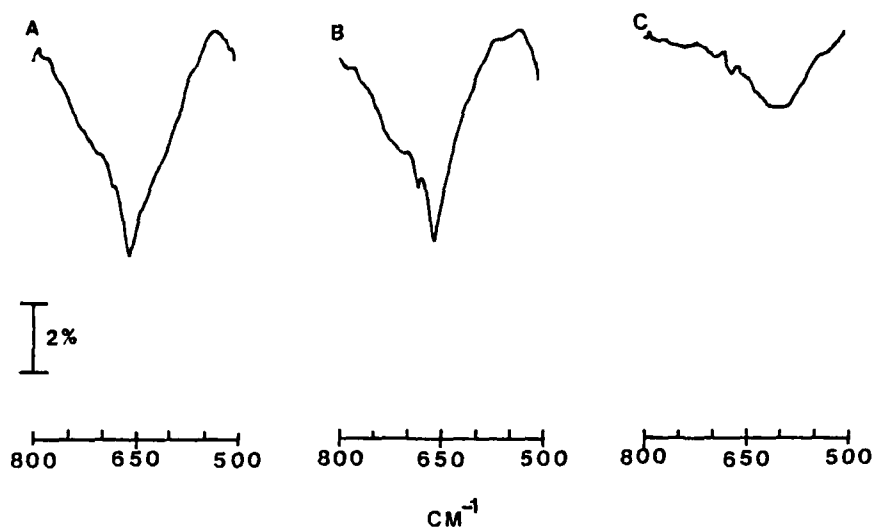
Figure 8. Effect of immersion in 1% aqueous solution of γ-APS at pH 10.4 on infrared spectra of oxide on iron mirrors: (A) - before immersion, (B) - after immersion for thirty minutes, and (C) - difference.

Figure 9. Effect of immersion in 1% aqueous solution of γ-APS at pH 8.0 on infrared spectra of oxide on iron mirrors: (A) - before immersion, (B) - after immersion for thirty minutes, and (C) - difference.

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Figure 10. Breaking strength versus immersion time in water at 60°C for iron/epoxy lap joints: (A) - no primer, (B) - γ-APS primer at pH 10.4, and (C) - γ-APS primer at pH 8.0.
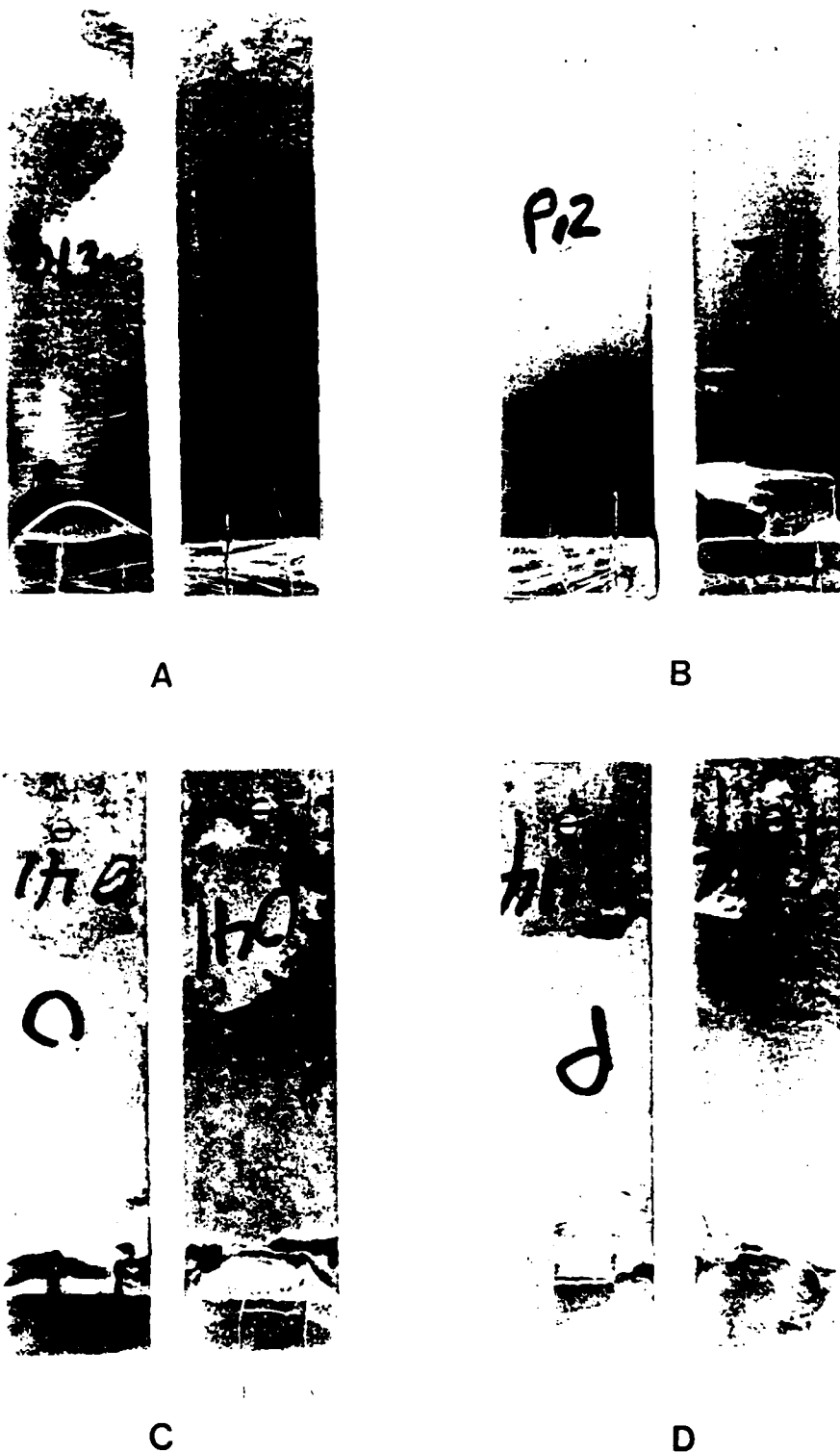
Figure 11. Fracture surfaces of iron/epoxy lap joints. Samples A (no primer) and B (γ-APS primer at pH 10.4) were fractured dry. Samples C (no primer) and D (γ-APS primer at pH 10.4) were fractured after 20 days in water at 60°C.
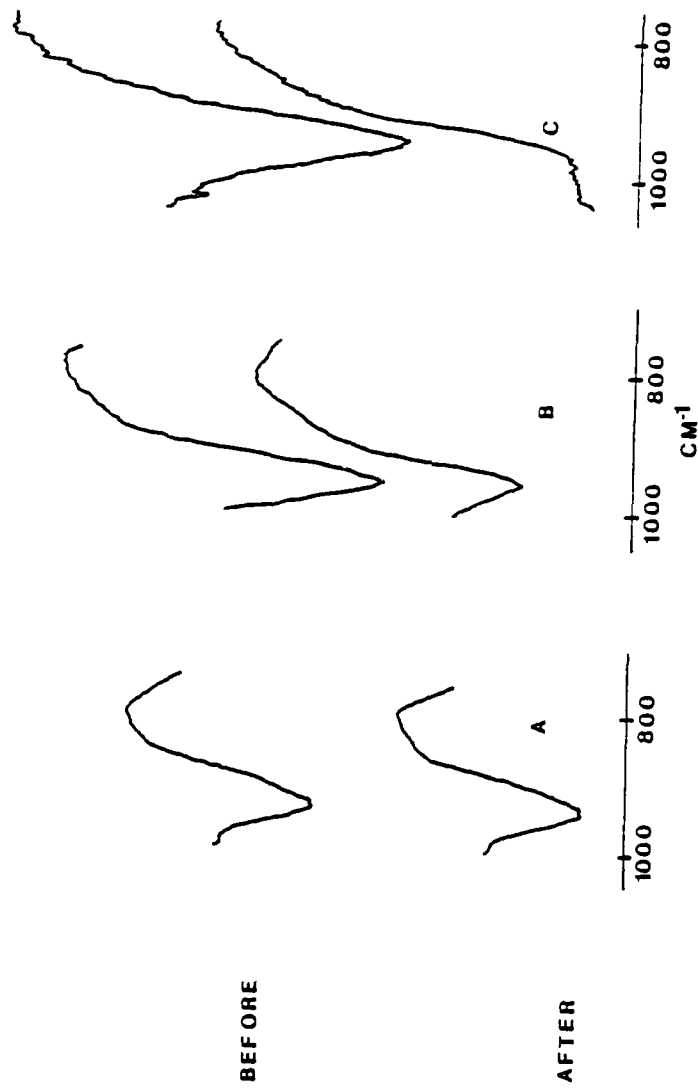
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Figure 12. Infrared spectra of aluminum oxides before and after immersion for 15 minutes in 1% aqueous solutions of γ-APS at (A) - pH 6.8, (B) - pH 8.5, and (C) - pH 10.4.
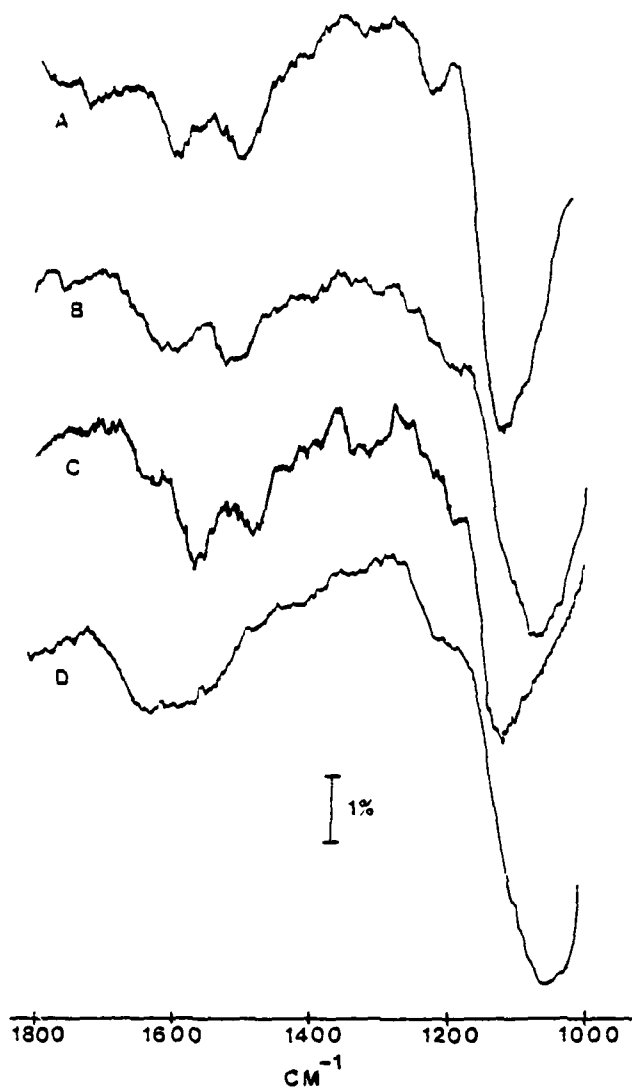
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Figure 13. Infrared spectra of thin films formed by γ-APS adsorbed onto aluminum from 1% aqueous solutions at (A) - pH 6.8, 15 minutes, (B) - pH 8.5, 15 minutes, (C) - pH 10.4, 1 minute, and (D) - pH 10.4, 15 minutes.
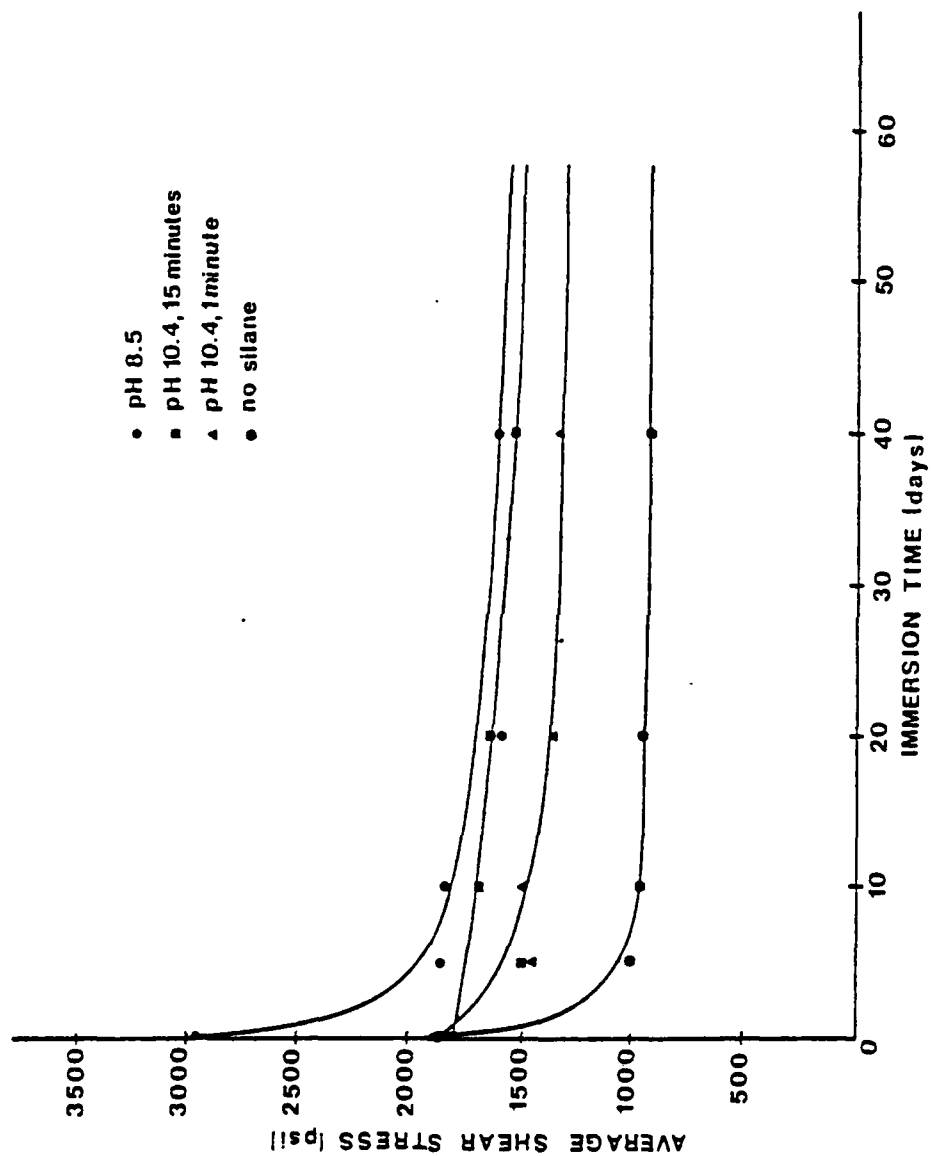
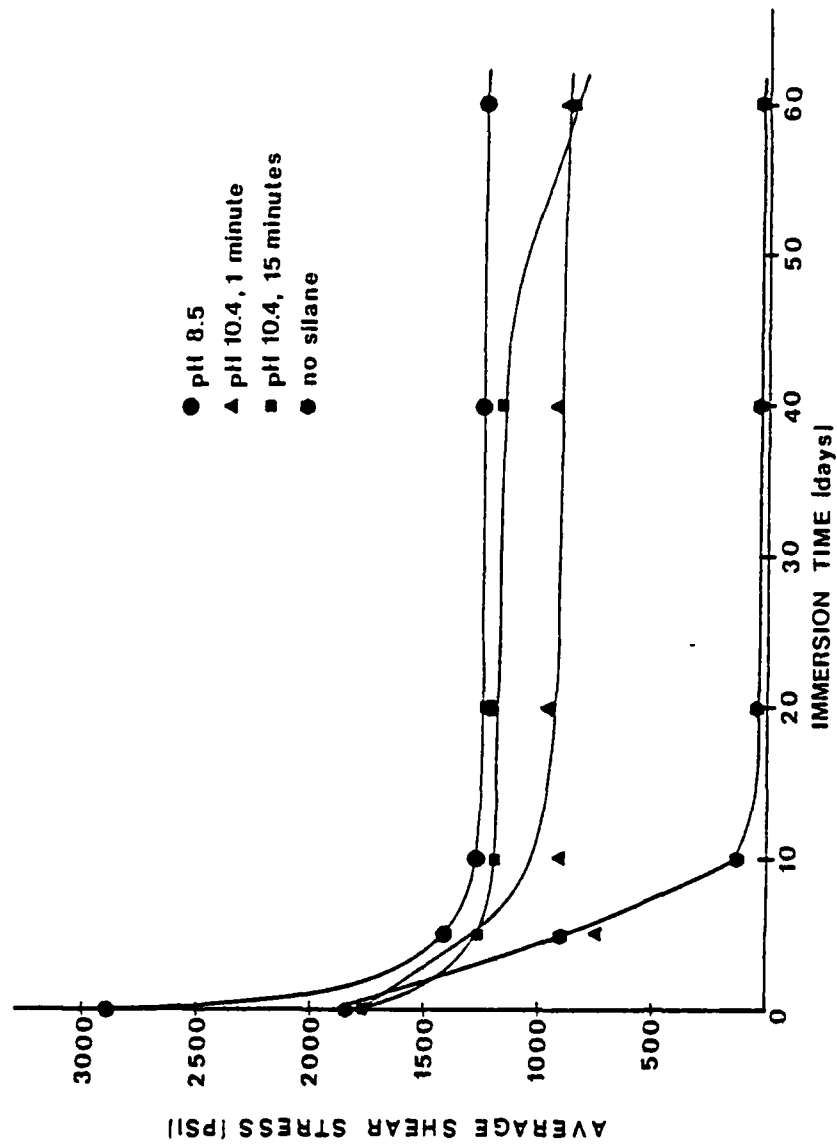Figure 14. Breaking strength versus immersion time in water a 60°C for aluminum/epoxy lap joints.

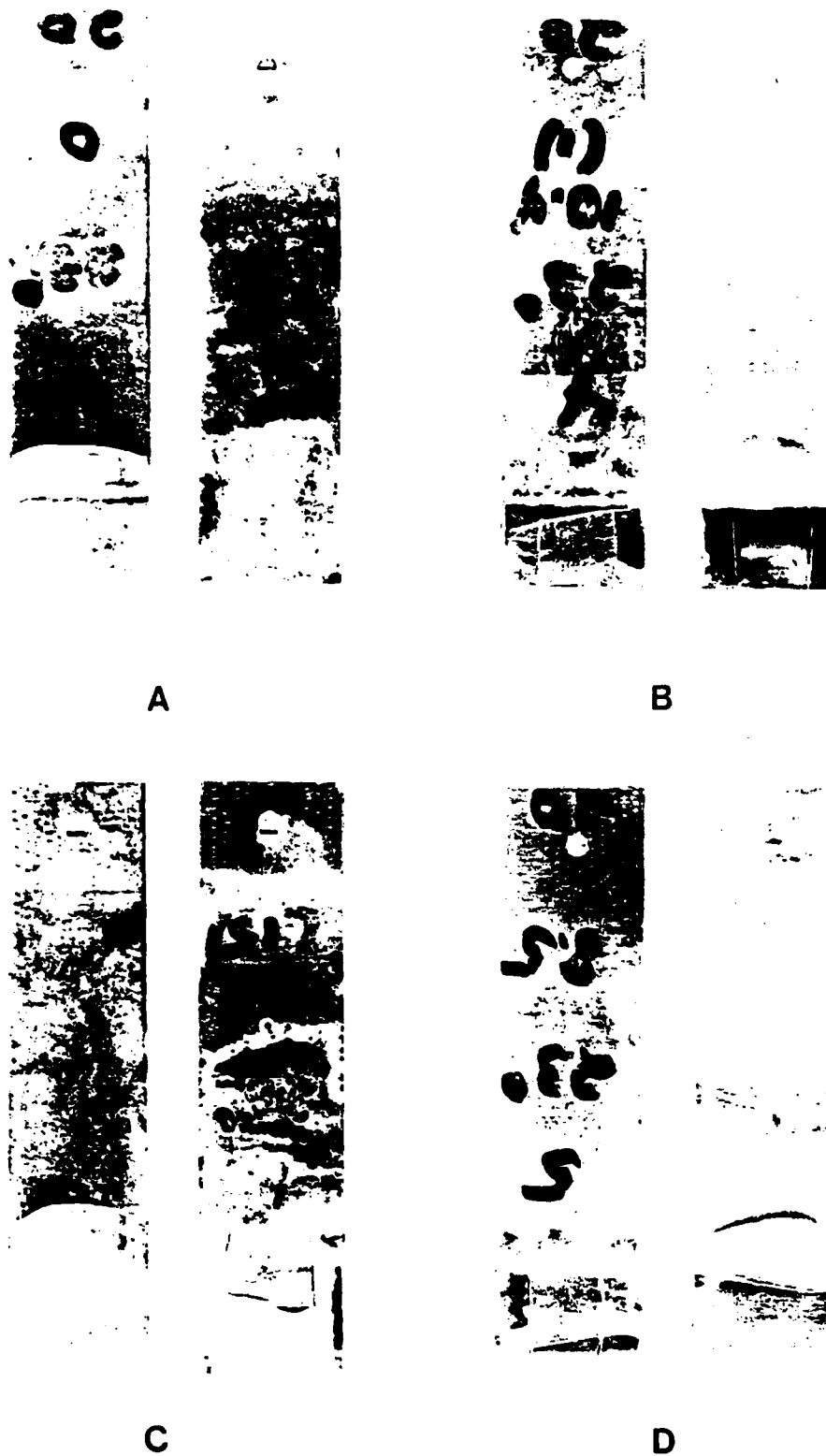Figure 15. Breaking strength versus immersion time in water at 23°C for aluminum/epoxy lap joints.

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Figure 16. Fracture surfaces of aluminum/epoxy lap joints after 40 days in water at 23°C: (A) - no primer, (B) - γ-APS at pH 10.4 for 1 minute, (C) - γ-APS at pH 10.4 for 15 minutes, and (D) - γ-APS at pH 8.5.

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